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Infrared ATR Spectra of Stearic Acid LB Films: Intensity Enhancement by Au Evaporation

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Band intensity enhancement in infrared ATR spectra of stearic acid LB films overcoated with Au films was studied by Fourier transform infrared spectroscopy. Principally, similar results with the case of evaporated Ag films [T. Kamata, A. Kato, J. Umemura, and T. Takenaka, *Langmuir*, to be published] was obtained, although the intensity enhancement was larger in this case than in the Ag film case if the metal thickness is the same. Besides the intensity enhancements of the absorption bands due to the reacted gold stearate species, those of the free C=O stretching band in 1-monolayer LB films and the hydrogen bonded dimeric C=O stretching band in multilayer LB films were observed. This may come from the fact that the Au film is chemically less reactive than the Ag film. These results indicate the importance of the electromagnetic field effect in the observed intensity enhancements.

KEY WORDS: FT-IR ATR spectra/ Stearic acid/ Langmuir-Blodgett film/ Intensity enhancement/ Gold metal/

INTRODUCTION

The discovery of surface enhanced Raman scattering (SERS) by Fleischmann *et al.*[1] in 1974 has stimulated wide interest in the interaction of electromagnetic wave with molecules adsorbed on metal surfaces.[2] Besides that, intensity enhancements of infrared attenuated total reflection (ATR) spectra[3-9] have been reported for organic molecules overcoated or undercoated with thin metal films. In a previous work,[10] we have studied intensity enhancements in infrared ATR spectra of Langmuir-Blodgett (LB) films of stearic acid overcoated with Ag films. In the case of 1-monolayer LB film, almost all stearic acids reacted with Ag forming silver stearate. The symmetric COO^- stretching band, whose transition moment is normal to the Ag surface, was most enhanced. It was revealed that only the electric field polarized parallel to the monolayer plane can enhance infrared absorptions of the monolayer, being consistent with the intensity enhancement due to the high electromagnetic field through collective electron resonances among small Ag islands.

Since these intensity enhancements are expected to be dependent on dielectric properties of metals, we herein expanded the study of this series to thin evaporated Au overlayers.

EXPERIMENTAL

Stearic acid used in this study is the same as that reported previously.[10,11] Stearic acid monolayers were transferred from the water surface onto a Ge ATR plate (Fig. 1) with transfer ratio of 0.97 ± 0.03 by the LB method,[12] as described previously.[10,11]

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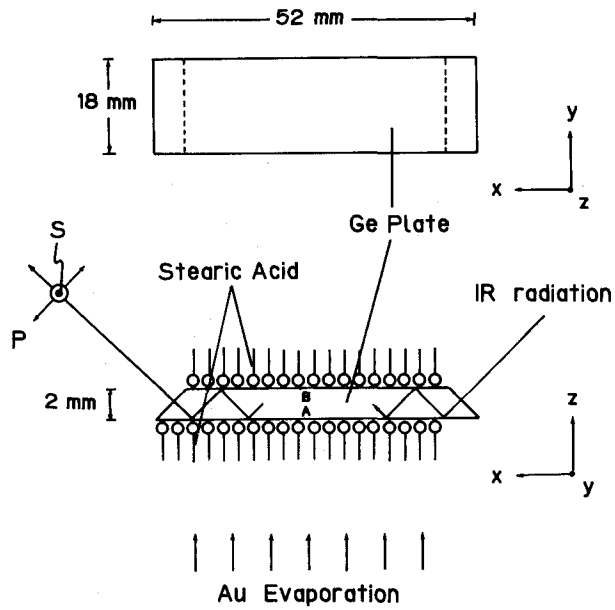


Fig. 1. Ge ATR plate and its coordinate system.

Granulated Au with *ca.* 2 mm diameter of 99.99% purity was purchased from Higuchi Chemical Co., Ltd. Au films with mass thicknesses from 0.5 to 3.5 nm were deposited on one large face (A) of the Ge plate with single and multiple stearic acid monolayers (Fig. 1) in an Ulvac Model EBH-6 vacuum evaporator at the rate of 6 nm/min under vacuum of 3×10^{-6} Torr. A tungsten boat was used as an evaporation source. The mass thickness of the Au film was evaluated by an Ulvac Model CRTM deposition monitor equipped with an oscillating quartz crystal.

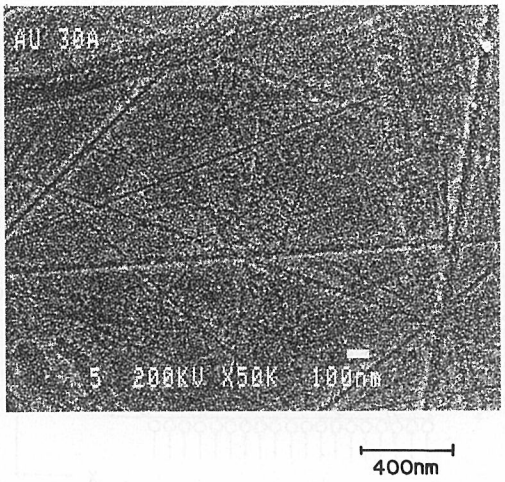
Polarized infrared ATR spectra with 4 cm^{-1} resolution were recorded on a Nicolet Model 6000C FT-IR spectrophotometer equipped with an MCT detector, a wire-grid polarizer, and a Perkin-Elmer 45° incidence multiple internal reflection attachment.[10,11] The number of scanning was 5000. Since the stearic acid monolayers were deposited on both sides (A and B in Fig. 1) of the Ge plate, while the Au film was evaporated only on one side (A), all spectra reported here were obtained by subtracting the spectra recorded for the same Ge plate with the same stearic acid monolayers only on the B side.

Scanning electron micrographs were taken by a JEOL Model JEM-2000FX electron microscope at an accelerating voltage of 200 KV.

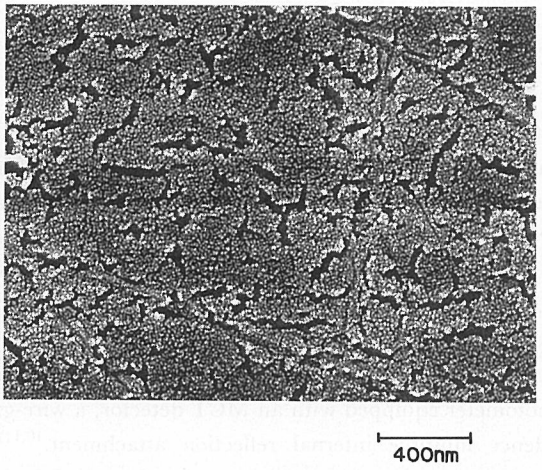
RESULTS AND DISCUSSION

Intensity enhancement in 1-monolayer LB film of stearic acid

Figure 2(A) is a scanning electron micrograph of a 3.0 nm Au film evaporated on a 1-monolayer LB film of stearic acid. It can be seen that the Au film consists of closely packed granular islands. The average diameter of the islands is *ca.* 8 nm, being much smaller than that of the Ag islands (30 nm) reported previously.[10]



(A)



(B)

Fig. 2. Scanning electron micrographs of 3.0 nm Au films evaporated on (A) 1-monolayer and (B) 7-monolayers stearic acid LB films on Ge plate. Many straight lines in (A) are scratches on the Ge surface.

Figure 3 shows the dependence of infrared reflectivity of the Ge plate on the Au film thickness. With increase in Au film thickness, the background reflectivity was markedly decreased from the high frequency side as a consequence of the absorption of Au island films. Thus, we used Au films thinner than 3.5 nm in this study. This limit was smaller than that (5 nm) of Ag island films.[10]

Figure 4 represents ATR spectra of the 1-monolayer LB films of stearic acid with various Au film thicknesses obtained by the p-polarized radiation which has the electric vector parallel to the plane of incindence. The same spectra with the identical intensity enhancement were obtained by the s-polarized radiation which has the electric vector perpendicular to the plane of incidence. Bands at 2961, 2920, and 2851 cm^{-1} are assigned to the asymmetric CH_3,

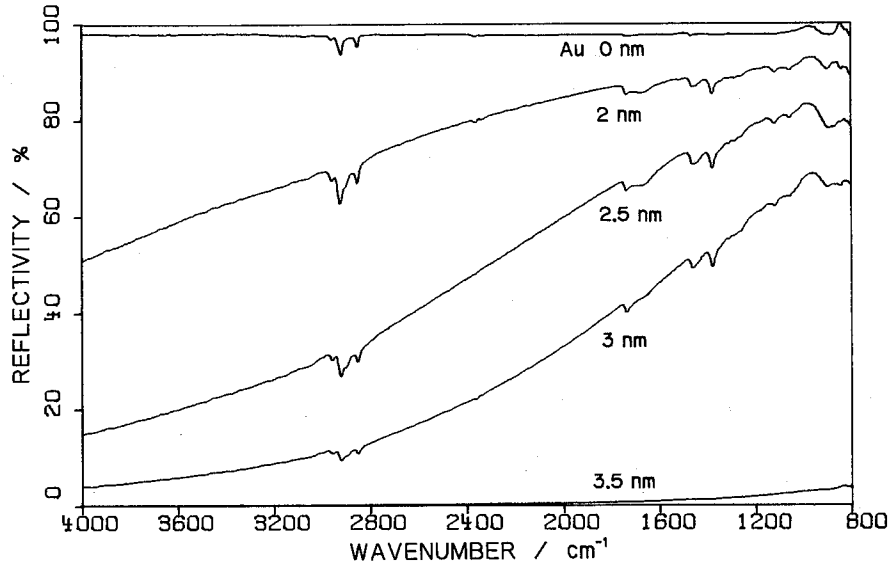


Fig. 3. Dependence of infrared reflectivity of Ge plates (with 1-monolayer stearic acid) on Au film thickness.

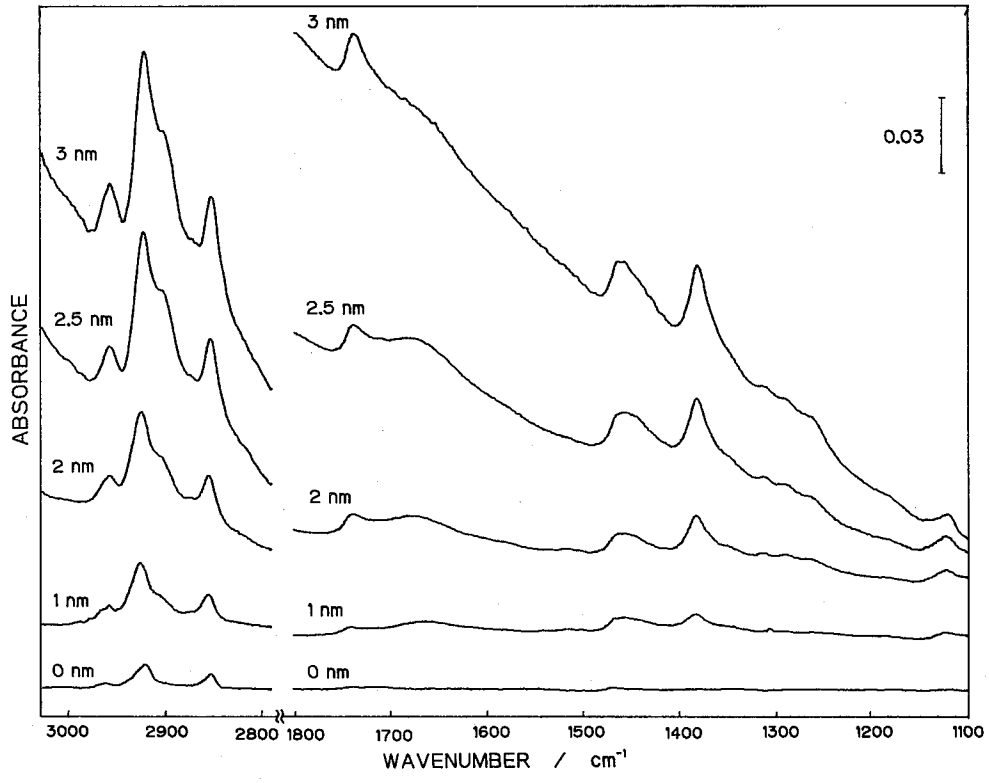


Fig. 4. p-Polarized infrared ATR spectra of 1-monolayer LB films of stearic acid with various Au film thicknesses.

antisymmetric CH_2 and symmetric CH_2 stretching vibrations, respectively. Bands at 1467 and 1120 cm^{-1} are due to the CH_2 scissoring and C–C strethching vibrations, respectively. Although their intensities are very weak before Au evaporation, they grew large with increasing Au film thickness. A shoulder band at 2900 cm^{-1} can be assigned to the overtone of the CH_2 scissoring band due to the *gauche* conformers[13] which was produced by Au deposition. In fact, upon this treatment, a broad band ascribed to the CH_2 scissoring mode of the *gauche* conformers appears around 1450 cm^{-1} as a shoulder of the 1467-cm^{-1} band which is due to the same mode of the *trans* conformer. A band at 1385 cm^{-1} can be assigned to the symmetric COO^- stretching vibration of the stearate ion on the Au island surface, like the 1395-cm^{-1} band of that on the Ag island surface.[10] This fact indicates that the evaporated Au islands are not simply on top of the hydrocarbon chains of the stearic acid monolayer, but come into contact and react with the carboxylic groups on the Ge surface,[10] Besides the carboxylate band, a band assignable to the non-hydrogen-bonded (free) C=O stretching mode of stearic acid,[14] appears at 1738 cm^{-1} and is subject to intensity enhancement due to Au evaporation. This band was very weakly observed in the case of Ag evaporation, and therefore it was not mentioned in the

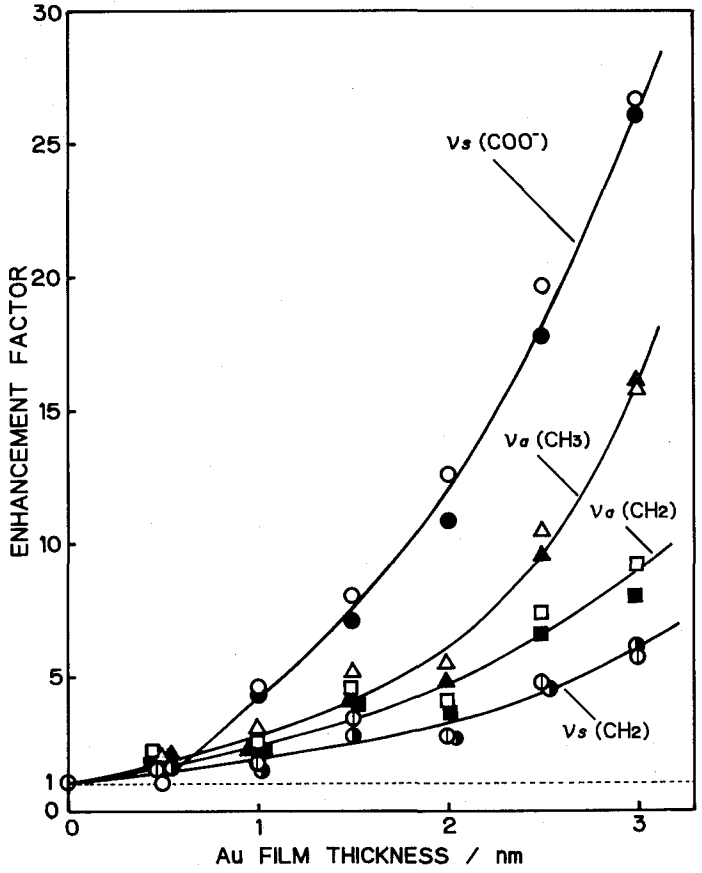


Fig. 5. Intensity enhancement factors for major absorption bands as functions of Au film thickness. Open and solid symbols refer to p- and s-polarized radiations, respectively.

previous paper.[10] In other words, Au less reacts with stearic acid to form stearate ion than Ag does, presumably because of a weaker ionization tendency of Au. It should be noticed that the presence and the intensity enhancement of the free C=O stretching band of stearic acid are indicative of the unnecessity of chemical adsorption to the intensity enhancement, which is often claimed as the origin of SERS.[2]

Intensity enhancement factors for major absorption bands derived from the data in Fig. 4 are shown in Fig. 5 as functions of Au film thickness. For the CH stretching bands, the enhancement factors were calculated on the basis of the corresponding band intensities obtained without Au. For the symmetric COO^- stretching band, however, it was based on the intensity obtained with the 0.5 nm Au film, since there was no band without Au. Enhancement factors at 3 nm Au thickness almost coincides with the corresponding factors at 4.5 nm Ag thickness.[10] This means that the enhancement by Au is larger than that by Ag, if the thickness is the same. In accord with the case of Ag evaporation,[10] the enhancement factors decrease with increasing the angle between the transition moment of the absorption band and the surface normal, if stearate ion is oriented with its hydrocarbon chain axis perpendicular to the Au surface.

In Fig. 5, enhancement factors for the p- and s-polarized radiations are practically the same. Furthermore, it was found that the normal incidence transmission spectra (the electric vector is parallel to the surface) of the stearic acid monolayer are largely enhanced upon Au evaporation, while the grazing incidence reflection-absorption spectra (the electric vector is perpendicular to the surface) of the same sample are not enhanced. As previously described in detail,[10] these facts indicate that the z component (Fig. 1) of the electric field for the evanescent wave in the p-polarized radiation is negligible, and the x component in the p-polarized radiation and the y-component (only one component) in the s-polarized radiation are the same.[7] In other words, the intensity enhancement is generated only by the electric field polarized parallel to the Ge surface. This may be due to the great enhancement of the local electromagnetic field in the gap between adjacent Au islands through the excitation of the collective electron resonances of the small metal islands[15] by irradiation of the incident light. Therefore, stearate ions located on the hills of the Au islands make little contribution to intensity enhancement, but those located at the edges of the Au islands make large contribution.[10]

The dependence of the enhancement factor for the free C=O stretching band of unreacted stearic acid on Au film thickness was the same order with those of the CH_2 stretching bands shown in Fig. 5. Since the direction of the transition moment of the free C=O stretching mode in the *cis* conformation[16,17] roughly coincides with that of the symmetric CH_2 stretching band, the hydrocarbon chain of the unreacted stearic acid also orients in a similar degree as that of the stearate ion on the edge surface of the Au islands.

Intensity enhancement in multilayer LB films of stearic acid

Figure 2 (B) is the scanning electron micrograph of a 3.0 nm Au film evaporated on the 7-monolayer LB film of stearic acid on the Ge plate. It also consists of closely packed granular islands with the average diameter of *ca.* 8 nm. As compared with the 1-monolayer LB film, the distribution of the islands is not uniform but there are many fissures where no island is found.

Figure 6 shows the p-polarized ATR spectra of the 1-, 3-, and 7-monolayer LB films before

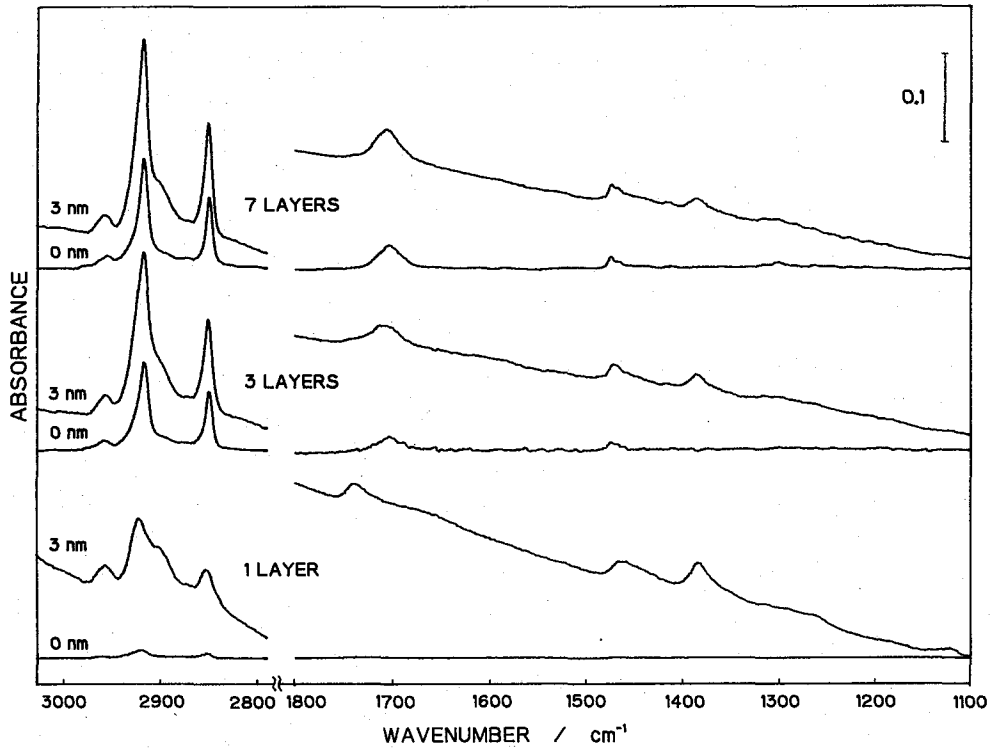


Fig. 6. p-Polarized infrared ATR spectra of 1-, 3-, and 7-monolayer LB films of stearic acid before and after evaporation of 3.0 nm Au film.

and after evaporation of the 3.0 nm Au film. Principally, the experimental results are similar to those of the 4.5 nm Ag evaporated films. Although the enhancement factor of the CH stretching bands in the 1-monolayer LB film is very large, it is small in the 7-monolayer LB film. Enhancement factors for the CH stretching bands are plotted in Fig. 7 against the number of monolayers. The decrease in enhancement factor with the number of monolayers is obvious, although slightly milder than the case of Ag film.[10] Therefore, it is considered that the intensity enhancement is most prominent for the vibration bands of stearate ion and stearic acid that are in contact with the edge of the Au islands. Further, the electromagnetic field intensity at the gap between the Au islands decreases with the number of monolayers, since separations between them are statistically increased. The intensity decrease in the symmetric COO^- stretching band with the increase in the number of monolayers (Fig. 6) can be understood by this mechanism.

In the 1700 cm^{-1} region of the infrared spectra in Fig. 6, there are two C=O stretching bands. One is the free C=O stretching band at 1738 cm^{-1} which appears in the 1-monolayer LB film as mentioned above, and the other is the C=O stretching band of the hydrogen-bonded dimer at 1702 cm^{-1} which appears in the multilayer LB films. The enhancement of the free C=O stretching band in the 1-monolayer LB film may indicate that evaporated Au atoms reach to the Ge surface where the C=O group exist as monomeric form. In the multilayer LB films, however, the intensity of the free C=O stretching band can hardly be

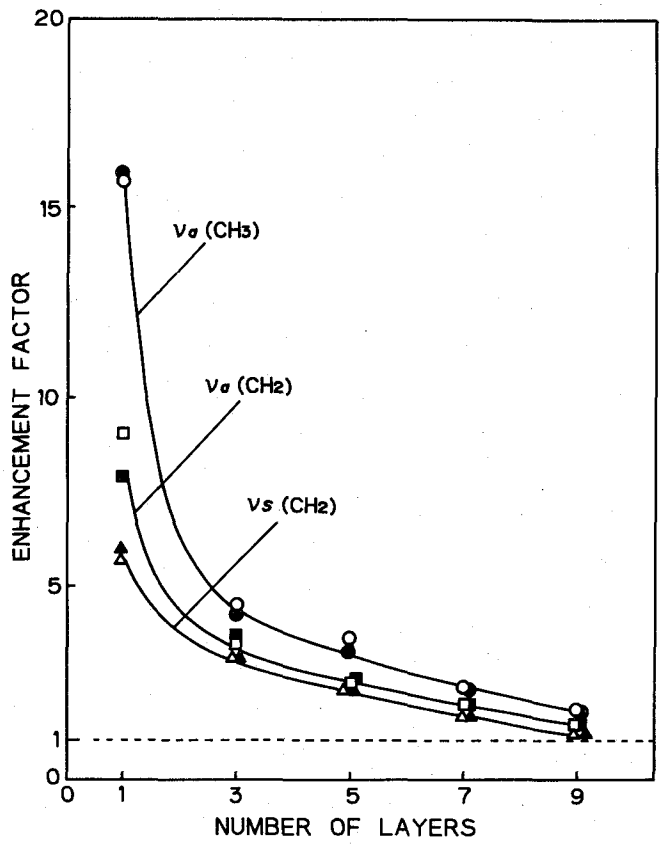


Fig. 7. Intensity enhancement factors for the CH stretching bands as functions of number of monolayers. Open and solid symbols refer to p- and s-polarized radiations, respectively.

seen. This means that Au atoms do not reach to the Ge surface. On the other hand, the C=O stretching band of the hydrogen-bonded dimer experiences intensity enhancement in multilayer LB films, especially in the 3-monolayer film. This fact indicates that evaporated Au atoms penetrate at least the outmost stearic acid monolayer into the layer of the carboxylic dimer rings. The intensity enhancement of this band was not obvious in the case of Ag film,[10] presumably due to the strong tendency of Ag to form stearate ions when the carboxylic group comes in proximity to the Ag surface.

As stated above, the shoulder band at 2900 cm^{-1} is due to the disordered hydrocarbon chain with the *gauche* conformation. The intensity of this band stays almost constant irrespective of the number of monolayers. This suggests that the disorder occurs at only local places where Au atoms collide upon evaporation.

In conclusion, the intensity enhancement of stearic acid LB films due to the Au evaporation is principally the same as that by Ag films. The Au film can enhance infrared absorption intensities with less film thickness than the Ag film. Au is chemically milder than Ag in its reactivity to form stearate ion. Therefore, the Au evaporation can be effectively used as a sensitive method to detect small amounts of surface species by means of infrared ATR

spectroscopy. Examination of the effect of several metals other than Ag and Au has been also performed and will be reported separately.[18)]

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